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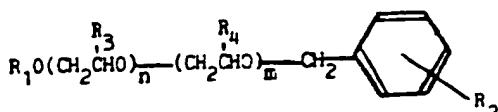
# UK Patent Application GB 2 158 080 A

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(54) End-blocked nonionic surfactants

(57) Alkylbenzyl poly(oxyalkylene) derivatives of the formula



wherein R<sub>1</sub> is a straight or branched chain 1–4C alkyl group; R<sub>2</sub> is a straight or branched chain 4–20C alkyl group; R<sub>3</sub> and R<sub>4</sub> are each, independently, H or CH<sub>3</sub>; n and m are each integers wherein n + m does not exceed 20 have good nonionic surface activity, biodegradability and are stable to caustic powders. The compounds are useful in alkaline cleaning compositions, such as dishwater products, and also in rinse-aid formulations for use in automatic dishwashers.

GB 2 158 080 /

## SPECIFICATION

## End-blocked nonionic surfactants

5 The present invention relates to end-blocked nonionic surfactants. More particularly, it relates to new alkylbenzyl poly(oxyalkylene) derivatives useful as nonionic surfactants. 5

In the past, a number of classes of compounds have been used, in detergents and janitorial compositions, as non-ionic surface active agents. Examples of these include amine ethoxylate propoxylates, benzyl-blocked alkylphenol alkoxylates and ethylene oxide-propylene oxide block copolymers. These materials 10 suffer the major disadvantage that they lack biodegradability and are unstable on solid caustic soda. Furthermore, such materials as are commercially available are ill-defined or have incompletely characteris- 10

able chemical structure.

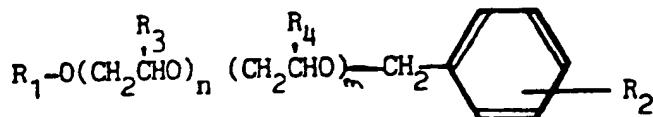
In an attempt to overcome the problem of lack of biodegradability of prior nonionic surfactants, alcohol ethoxylate propoxylates, having molecular weights less than 1000, were used. Unfortunately, these 15

materials have poor dispersibility in water at temperatures above their cloud points. In addition, they are 15 unstable in the presence of solid caustic powders, e.g. caustic soda, as in the case of the earlier nonionics.

Further attempts to overcome the drawbacks of the prior art materials involved "blocking" the terminal hydroxyl group in fatty alcohol ethoxylates with alkyl chlorides. The procedures used, however, were difficult and they made use of toxic and expensive materials. Similarly blocked non-ionics using benzyl 20 chloride as alkylating agent were introduced although the commercial product was only about 70% blocked, 20 indicating the poor efficiency of the blocking procedure.

We have now discovered a range of compounds having good nonionic surface activity which are biodegradable and stable to caustic powders. Furthermore, we have discovered that these compounds can be prepared by a process which achieves greater than 90% blocking.

25 The present invention provides new compounds which are represented by the following general formula I. 25

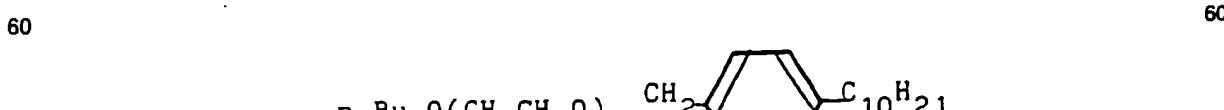
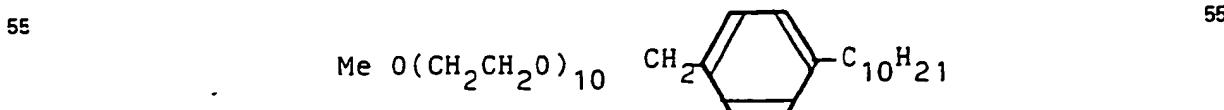
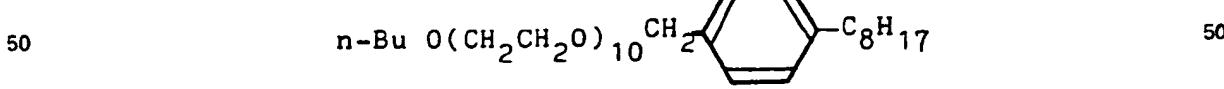
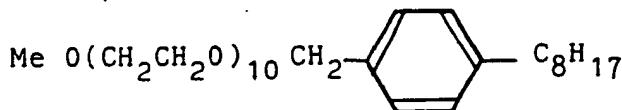


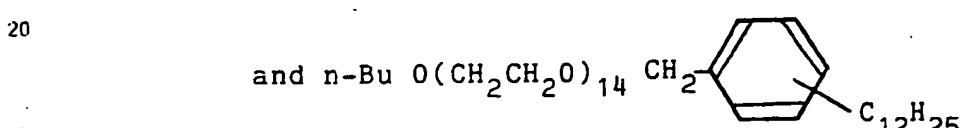
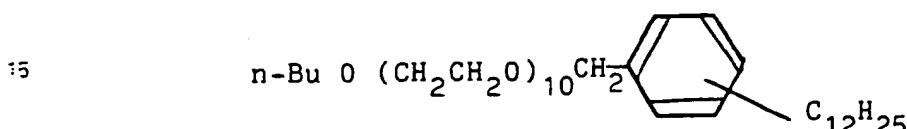
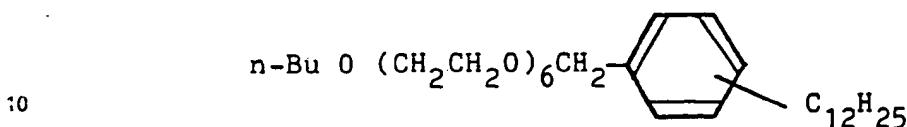
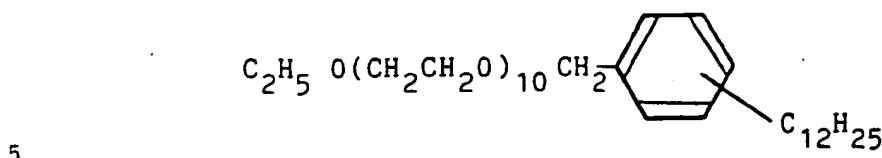
30 wherein  $R_1$  is a straight or branched chain alkyl group having from 1 to 4 carbon atoms;  $R_2$  is a straight or branched chain alkyl group having from 4 to 20 carbon atoms;  $R_3$  and  $R_4$  are each, independently, H or  $-CH_3$ , and  $n$  and  $m$  are each integers wherein the sum  $n + m$  is not greater than 20. 30

As we have stated above, the group  $R_1$  is a 1 to 4 C alkyl, such as methyl, ethyl, propyl, isopropyl, n-butyl, 35 isobutyl, sec-butyl and tert-butyl. The alkyl group  $R_2$  attached to the phenyl ring of the blocking group is a straight or branched chain group containing from 4 to 20 carbon atoms, preferably 8 to 12 carbon atoms. Preferred examples of suitable  $R_2$  groups include straight and branched chain octyl, decyl and dodecyl groups. A particularly preferred  $R_2$  group is n-dodecyl. 35

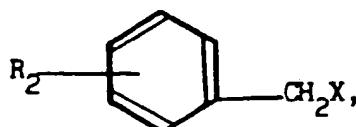
The sum  $n + m$  is not greater than 20 and will usually lie within the range of from 5 to 15, more particularly 40 within the range 8 to 14. A preferred value of  $n + m$  is 10. 40

Some preferred compounds of the present invention are as follows:





25 The present invention also provides a process for preparing a compound of the formula I above which process comprises reacting a lower alcohol of the formula  $R_1OH$ , wherein  $R_1$  is as defined above, with an alkylene oxide selected from ethylene oxide and propylene oxide, and then reacting the ethoxylated and/or propoxylated material with an alkylbenzyl halide having the formula



35 wherein X is a halogen atom, preferably a chlorine atom. In a preferred embodiment, the ethoxylated and/or propoxylated material is reacted with a mixture of alkylbenzyl chlorides, such as a mixture of C<sub>8</sub> and C<sub>10</sub> alkylbenzyl chlorides to give a mixture of reaction products.

If it is desired to form a compound of formula I wherein R<sub>3</sub> is H and R<sub>4</sub> is -CH<sub>3</sub>, then the lower alcohol is first reacted with ethylene oxide and the ethoxylated product is then reacted with propylene oxide. If the desired compound of formula I has R<sub>3</sub>=CH<sub>3</sub> and R<sub>4</sub>=H, then the alcohol is first propoxylated and the alkyl propoxylate is then ethoxylated. The amount of reactants used in this step, of course, depend upon the desired values of n and m in the final compound. Usually, the amounts of alkylene oxide used will be sufficient such that the sum of n + m is within the range of from 5 to 15. The alkoxylated lower alcohol is then condensed with the alkylbenzyl chloride. The condensation reaction will usually be conducted in the presence of an alkali metal hydroxide, typically NaOH. The condensation reaction is preferably phase transfer catalysed with, for instance, a catalytic amount of a tetraalkyl ammonium halide. By the use of this process, it is possible to achieve a blocking efficiency of greater than 90%. Furthermore, it should be noticed that, in the above-described process, end-blocking of the molecule and the introduction of the hydrophobe into the molecule are carried out in one step unlike prior art processes. Thus, by the process of the invention, it is possible to make end blocked non ionics at low cost.

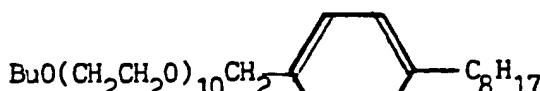
The compounds of the invention have relatively low molecular weight and meet E.E.C. legislation on biodegradability (Directive 82/242/EEC). They are stable on solid caustic powders and have excellent defoaming properties, good wetting and detergency. The compounds of the invention are, therefore, particularly well suited to use in strongly alkaline cleaning compositions in combination with solid caustic powders, such as powdered caustic soda. In particular, the compounds of the present invention are especially useful as low-foaming or anti-foaming ingredients in alkaline powder dishwashing products. They may also be used advantageously in rinse-aid formulations for automatic dishwashing and may control or prevent foam generated by destabilized food soils.

### *Example 1*

**Example 1**  
1 mole of n-butanol was ethoxylated with 10 moles of ethylene oxide by a conventional method. The ethoxylated product (150 g) was then charged together with 50% caustic soda solution (80 g) and, as catalyst, benzyltriethylammonium chloride (2.5 g). The temperature of this mixture was raised to 90-95°C at which temperature a mixture of *n*-octyl and *n*-decylbenzyl chloride (45 g) was run in over a period of 3 hours. The

reaction mixture was then heated to 110°C and maintained at that temperature for 1 hour. After cooling, the reaction mixture was washed with water to remove salt, unreacted polyglycol and catalyst. The product comprised a mixture of:-

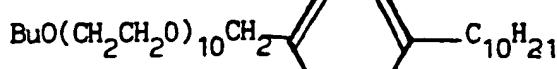
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and

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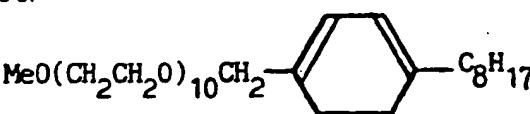
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*Example 2*

15 The procedure of Example 1 was repeated, except that methanol, instead of n-butanol, was used. The product comprised a mixture of

15

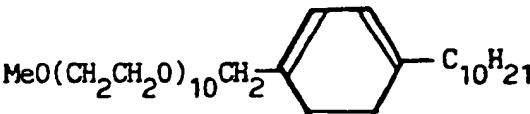
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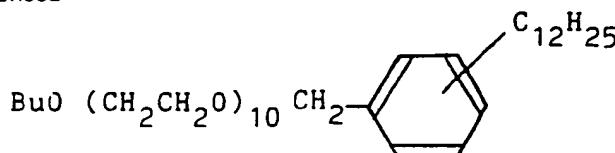
*Example 3*

30 The procedure of Example 1 was repeated except that dodecyl benzyl chloride, instead of p-octyl and p-decyl benzyl chloride, was used.

30

The product comprised

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40 Some of the properties of the products obtained in Examples 1, (A), and 2, (B), were measured and compared with those obtained for a prior art unblocked non-ionic surfactant, nonyl phenol 9.5 mole 40 ethoxylate (NP 95). These are set out below.

40

		A	B	NP95	
45	1.	Cloud point, at concentration of 1% in water, in °C	34	47	52
	2.	Foam (by Ross Miles), at a concentration of 0.1% in water and temperature 5°C below cloud point, in mm.	41	61	100
50	3.	Foam at cloud point, at concentration of 0.1% in water, in mm.	30	28	66
	4.	Wetting (by Draves) at a concentration of 0.1% in water and temperature 5°C below cloud point, in seconds	11 good	21 good	4 very poor.
55	5.	Stability on caustic			55

These results show that the compositions A and B, which are in accordance with the present invention, 60 show a big foam reduction compared to the prior art compound and suffer only small loss in wetting properties.

60

The compounds of this invention are advantageously used as low-foaming or antifoaming ingredients in alkaline powder dishwashing products.

**Example 4**

An alkaline powder dishwashing product with good cleaning power and controlled foaming characteristics is prepared by blending the following:

5	Sodium metasilicate	30%	by weight	5
	Soda ash	38%	by weight	
	*Trisodium nitrilo triacetic acid powder	10%	by weight	
	Sodium tripolyphosphate	20%	by weight	
	Suitable compound of present invention	2%	by weight	

10 \*e.g. Nervanaid NTA Conc. Powder, a trade name of A.B.M. Chemicals Ltd.

10

wherein the suitable compound of the present invention is one or a mixture of more than one of the following:

- 15 a) A compound according to formula 1 wherein  
 $(n + m) = 10$  and  
 $R_3 = R_4 = H$  and  $R_1 = C_2H_5$  and  $R_2 = C_{12}H_{25}$
- b) a compound according to formula 1 wherein  
20  $(n + m) = 6$  and  
 $R_3 = R_4 = H$  and  $R_1 = C_4H_9$  (n-butyl) and  $R_2 = C_{12}H_{25}$
- c) a compound according to formula 1 wherein  
25  $(n + m) = 14$  and  
 $R_3 = R_4 = H$  and  $R_1 = C_4H_9$  (n-butyl)  
and  $R_2 = C_{12}H_{25}$ .

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The compounds of the invention are advantageously used in rinse-aid formulations for automatic dishwashing. Spotless quick-drying is achieved without causing subsequent foaming problems in those machines where rinse water is re-cycled into the wash-water. Furthermore formulations containing compounds of the present invention may control or prevent foam generated or stabilised by food soils.

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**Example 5**  
Rinse aid formulations for automatic dishwashing according to the following recipes give spotless quick-drying:

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	Suitable compound of present invention	25%
	Dipropylene glycol	10%
	N-lauroyl sarcosinate	1%
40	Water	64%

40

Where a suitable compound of the present invention includes a mixture of compounds according to formula 1, wherein, for example,  $(n + m) = 6$  and  $14$  and  $R_3 = R_4 = H$  and  $R_1 = C_4H_9$  (n-butyl) and  $R_2 = C_{12}H_{25}$ . Such mixture comprises 60% of such compound wherein  $(n + m) = 14$  and 40% of such compound wherein  $(n + m) = 6$ , and when the formulation of Example 5 is made with this mixture of non-ionic surface active agents a formulation (Formulation 1) with properties superior to those of current commercial formulations is obtained, as measured in the following tests:

45

	Actives % (Drying at 110°C)	Protein* Foam (mm)	Haze Temp. (°C)	Dispersibility in water at 80°C	Glass rinse appearanc at 80°C	50
50	Formulation 1	36	24	61	Excellent	Excellent
55	Commercial Product A	30	184	51	Fair	Very good
	Commercial Product B	50	50	60	Good	Fair
	Commercial Product C	32	90	47	Good	Fair

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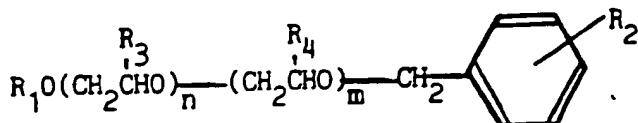
60 \* Protein foam tests measure the height of foam produced in a dynamic foaming test with 100 ppm of rinse aid in water of 150 ppm hardness in the presence of 0.25% milk protein and 0.36% alkaline builders at a temperature of 60°C. The test involves pumping the test solution at a pressure of 5 psi through a 1.8 mm orifice with a fall of 750 mm onto the surface of the test solution with recirculation for 5 min.

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## CLAIMS

1. A compound which is represented by the following general formula:-

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10 wherein  $\text{R}_1$  is a straight or branched chain 1-4C alkyl group;  $\text{R}_2$  is a straight or branched chain 4-20C alkyl group;  $\text{R}_3$  and  $\text{R}_4$  are each, independently, H or  $-\text{CH}_3$ ; and  $n$  and  $m$  are each integers wherein the sum  $n + m$  is not greater than 20.

15 2. A compound as claimed in claim 1, wherein  $\text{R}_2$  is a straight or branched chain alkyl group having from 8 to 12 carbon atoms.

15 3. A compound as claimed in claim 2, wherein  $\text{R}_2$  is a straight or branched chain octyl, decyl or dodecyl group.

4. A compound as claimed in any one of claims 1 to 3, wherein the sum of  $n + m$  is in the range of from 5 to 15.

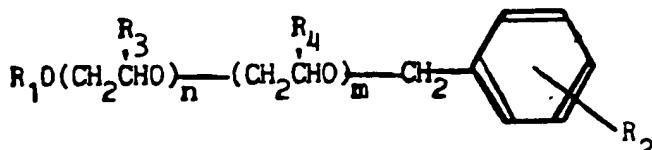
5. A compound as claimed in any one of claims 1 to 4, wherein  $\text{R}_1$  is n-butyl;  $\text{R}_2$  is a substantially linear 20 dodecyl;  $\text{R}_3$  and  $\text{R}_4$  are both H and the sum  $n + m$  is in the range of from 5 to 15.

20

6. A compound as claimed in any one of claims 1 to 4, wherein  $\text{R}_1$  is ethyl;  $\text{R}_2$  is a substantially linear dodecyl;  $\text{R}_3$  and  $\text{R}_4$  are both H and the sum  $n + m$  is in the range of from 5 to 15.

7. A method of preparing a compound having the following general formula:-

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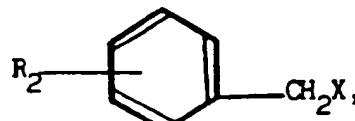
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30 wherein  $\text{R}_1$  is a straight or branched chain 1-4C alkyl group;  $\text{R}_2$  is a straight or branched chain 4-20C alkyl group;  $\text{R}_3$  and  $\text{R}_4$  are each, independently, H or  $-\text{CH}_3$ ; and  $n$  and  $m$  are each integers wherein the sum  $n + m$  is not greater than 20,

35 which method comprises reacting an alcohol of the formula  $\text{R}_1\text{OH}$ , where  $\text{R}_1$  is as defined above, with an alkylene oxide selected from ethylene oxide, propylene oxide and mixtures thereof and then reacting the resulting alkoxylated material with an alkylbenzyl halide having the formula

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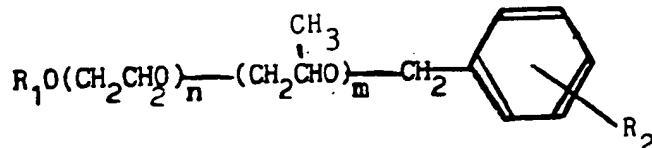


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wherein  $\text{R}_2$  is as defined above and  $X$  is a halogen atom.

8. A method of preparing a compound having the following general formula:-

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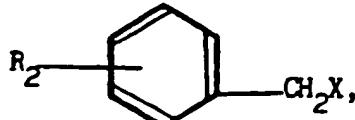


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50 wherein  $\text{R}_1$  is a straight or branched chain 1-4C alkyl group;  $\text{R}_2$  is a straight or branched chain 4-20C alkyl group; and  $n$  and  $m$  are each integers wherein the sum  $n + m$  is not greater than 20, which method comprises reacting an alcohol of the formula  $\text{R}_1\text{OH}$ , where  $\text{R}_1$  is as defined above, with ethylene oxide, then reacting the resulting ethoxylated product with propylene oxide and then reacting the resulting propoxylated material with an alkylbenzyl halide of the formula:-

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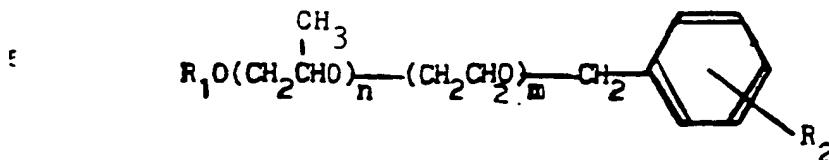
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where R<sub>2</sub> is as defined above and X is a halogen atom.

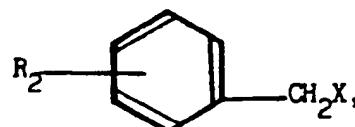
9. A method of preparing a compound having the following general formula:-



10. wherein R<sub>1</sub> is a straight or branched chain 1-4C alkyl group; R<sub>2</sub> is a straight or branched chain 4-20C alkyl group; and n and m are each integers wherein the sum n + m is not greater than 20, which method comprises reacting an alcohol of the formula R<sub>1</sub>OH, where R<sub>1</sub> is as defined above, with propylene oxide, reacting the resulting propoxylated material with ethylene oxide and then reacting the resulting ethoxylated product with an alkylbenzyl halide of the formula

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wherein R<sub>2</sub> is as defined above and X is a halogen atom.

10. A cleaning composition comprising a mixture of caustic soda and at least one compound as claimed in claim 1.

11. A cleaning composition substantially as hereinbefore described in Example 4.

25. 12. A rinse aid formulation for use in an automatic dishwasher substantially as hereinbefore described in Example 5.

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